

CAPE COD RESEARCH
19 RESEARCH ROAD
EAST FALMOUTH, MA 02536



TELEPHONE (508) 540-4400
FAX (508) 540-4428

Thermoelectric Organics

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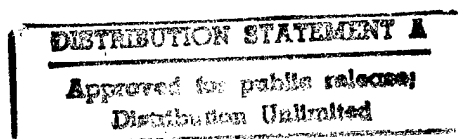
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19 Research Road
East Falmouth, MA 02536

Edgar Lazaro, Murty Bhamidipati, Matt Aldissi, & Brian Dixon

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Thermoelectric Organics

Summary

The research effort described herein investigated the feasibility of developing hybrid organic-inorganic compositions that possess superior thermoelectric properties. The results have identified composite materials in which very high Seebeck coefficients of up to 1000 microV/K have been coupled with very good electrical conductivities. A key goal of the Phase II effort was to increase the electrical conductivities, which was achieved. It was hoped that the very high Seebeck coefficients would not be affected by an increase in electrical conductivity. However, upon achieving conductivities of the order of 4.5 S/cm, the Seebeck dropped dramatically to very low or non-measurable levels. That is, although close to metallic conductivities were attained the corresponding zT was not improved. On the positive side the compositions were easily processed. In addition, computational modeling studies correlated electrical properties with molecular structure in a predictive manner.

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1.0 INTRODUCTION

The Phase II research conducted was an extension of the SBIR Phase I Topic A94-021 titled, *Advanced Thermoelectric Materials for Refrigeration and Cryogenic Cooling Systems*. The ultimate goal of this research was to develop hybrid organic-inorganic materials that possess superior thermoelectric properties.

In principle, thermoelectric devices have a number of inherent advantages over traditional heating and cooling technologies. Since they have no moving parts, their long term performance and durability are impressive. In principle, they could be compact and be fabricated into wide range of shapes. To date, what has limited their widespread application is their relatively poor Carnot efficiency. This efficiency is measure via a dimensionless figure of merit, ZT determined from the following classical equation:¹

$$ZT = S^2 \sigma T / k$$

Here T is the temperature in degrees Kelvin, S is the thermopower (Seebeck coefficient), σ is the electrical conductivity, and k is the thermal conductivity of the material of interest. The latter three parameters are inherent properties for any given material, however; they are also interrelated in a complex fashion. State of the art thermoelectric materials have $ZT \sim 1$ wherein $S \sim 200 \mu V/K$, $\sigma \sim 1000 S/cm$, and $k \sim 1-2 \times 10^{-2} W/cm-K$.² These materials are polycrystalline semiconductors based upon bismuth telluride alloys that have anisotropic thermoelectric properties. They are expensive and difficult to fabricate. Although devices based upon these brittle alloys have found use in specialized applications, they are not efficient enough to replace the large scale heating and cooling applications such as refrigeration, currently fulfilled by vapor-cycle devices. Moreover, although incremental improvements in the Carnot efficiencies ($ZT \sim 1-2$) of inorganic semiconducting thermoelectrics can be anticipated, larger improvements cannot.² This conclusion is reinforced by the fact that the value of ZT with crystalline inorganic species has been stuck at a maximum of ~ 1 for thirty years. In addition, the complexities of their fabrication will always limit their range of application, and keep their relative costs high. For thermoelectrics to have a dramatic impact upon non-specialty thermal management technologies, a new direction in dimensional materials is required. Such a new direction has been investigated during this Phase II work. The results have shown the thermoelectric promise of new dimensional organic-inorganic hybrid materials, but also the promise of ease of fabrication.

2.0 SIGNIFICANCE OF THE PHASE II WORK

While the feasibility work in the Phase I identified a novel and promising thermoelectric concept, a great deal of research and development must be carried out to define the parameters which control the thermal and electrical properties in a more exact fashion. The general approach of this Phase II research was to use dimensional organic-inorganic hybrid compositions to increase the thermal efficiency of thermoelectric materials to the point where thermoelectric cooling would largely replace conventional refrigeration and cooling systems. Basically, this involved investigating many different types of conducting polymer-template composites in a systematic manner to determine which variables control and optimize the thermoelectric performance.

2.1 Highlights of the Phase II Work

The Phase II results are summarized in this section which is followed by a detailed description of the experimental program. The following key points were established from the Phase II research:

- * Highly stable and reproducible thermopower values of -500 to -800 $\mu\text{V/K}$ were consistently obtained.
- * Highly conducting polymers layered with inorganic materials lower the Seebeck coefficient dramatically.
- * The relationship between the electron transport properties of the materials (i.e., electrical conductivity and Seebeck coefficient, and thermal conductivity) is highly complex.
- * The thickness of materials dramatically affects the thermoelectric properties.
- * The materials were easily processable and the thicknesses of layered materials can be accurately controlled.
- * Molecular modeling was used to correlate electrical conductivity with polymer/dopant structures.

3.0 PHASE II WORK CARRIED OUT

The primary objective of the Phase II research effort was to expand upon the promising leads uncovered during Phase I through the development of dimensional or superlattice structures possessing thermoelectric and processability properties superior to state of the art thermoelectric materials. It was hoped that by combining the well known and interesting electrical conductivities of conducting polymers with the induced structural ordering of inorganic material, such as vanadium oxide, that enhanced thermoelectric properties would be obtained. The following sections detail the technical approach and work performed to accomplish these tasks.

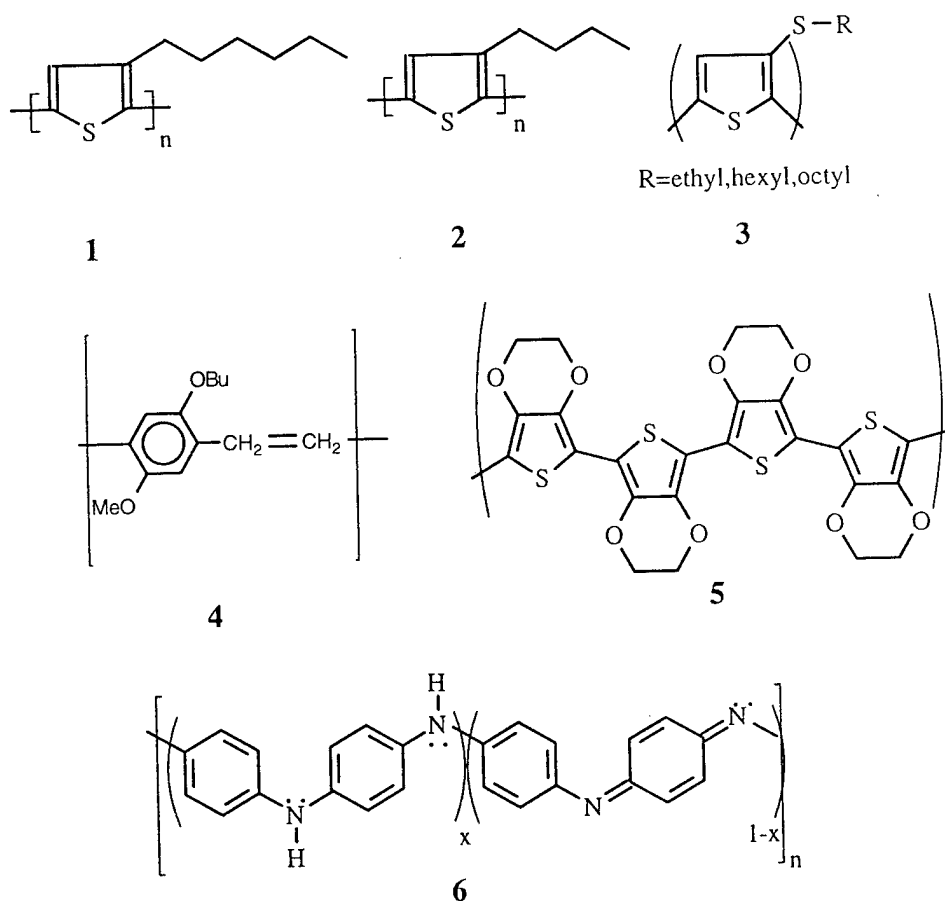
There were a large number of experimental variables in this research. The complex nature of the thermoelectric phenomena made it difficult to know which were the most critical in terms of performance optimization, but computer modeling of the polymer/dopant/inorganic phase structures gave important leads. A number of different experimental approaches were investigated. They are covered in no particular order of importance, but are all interrelated.

The thermoelectric phenomena is a complex one with many variables and trade-offs. The vast majority of past and present research efforts have revolved around the southeastern corner of the periodic table, especially bismuth based alloys of various kinds. However, the fact that the maximum ZT has hovered around a value of ~ 1 for the past thirty years, in spite of intensive research, suggests new research directions and novel material compositions should be sought. Our effort involves the exploration of dimensional organic-inorganic hybrid materials for advanced thermoelectric properties. More specifically, the technology of organic conducting polymers hybridized with layered, or dimensional, inorganic structures in an attempt to yield advanced thermoelectric materials. The primary thrust of this research was to significantly raise the electrical conductivity of the composites, while retaining the excellent n-type Seebeck coefficient values identified during Phase I. The former goal was achieved, however, at the expense of the high Seebeck numbers.

3.1 Experimental Results

3.1.1 Intrinsically Conducting Polymers

The Phase I dealt primarily with polythiophenes, for the Phase II program the scope was expanded to include other state of the art polymer systems including variously substituted polyanilines, and polyphenylenevinylenes. A large number of potential monomers are already known and they were synthesized and evaluated during this program. Below are the structures that we examined.



As introduced in the Phase I, work continued with **1** and **2**, poly(3-butylthiophene) and poly(3-hexylthiophene) respectively, but was also expanded to include **3**, poly(3-(alkylthio)thiophenes) which have reported conductivities around 200-700 S/cm.

Poly(phenylene vinylene), **4**, was a promising candidate because it's precursor is water soluble, and it has been reported to yield high electrical conductivity values. It also is known to readily form composites with inorganic hosts. Poly(ethylenedioxythiophene), **5**,

was used because of its high conductivity and commercial availability. Finally, 6, polyaniline, in its various conducting states was examined due to its excellent conductivity and relative ease of processability.

The important basic requirements for these polymers included the following: environmental stability, high conductivities in the undoped form (semiconductors), high conductivities in the doped (metallic) form, ease of fabrication and processability, and low thermal conductivity. A variety of polymerization techniques were used with an emphasis on producing pure conducting polymer films whose thickness can be carefully controlled.

3.1.2 Dimensional Templates and Hosts

The Phase II research dealt primarily with the vanadium oxide xerogel as an orienting matrix, an interesting material that yielded superb thermopower numbers and semiconducting conductivities by itself. Two methods to synthesize vanadium oxide were employed, the primary method by Lemerle, et al.,¹ as used in the Phase I and a method by Sanchez, et al.² The ultimate goal of the Phase II was to develop organized assemblies, in this case intrinsically conducting polymers intercalated within vanadium oxide xerogels, or other inorganic host material, that would be highly processable, and exhibit high ZT values.

There are a couple of important points to be considered in this structure, besides the obvious importance of the $VxOy$ and thiophene chemistries. The presence and amount of water that remains after the thiophene molecules intercalate has an important effect on the polymerization process as well as the composite's final properties. It is known that some of these water molecules are displaced as the monomers intercalate. In addition, the intercalation process changes the gallery height within some range, with corresponding effects upon the electronic properties.

An obvious second and closely related template material is the corresponding molybdenum oxide xerogel, MoO_3 . In the case of this xerogel, a wider range of gallery heights is known, thus larger monomers should fit in and be polymerizable. This xerogel has semiconducting properties similar to those of the vanadium case. In addition to these materials, $LiMoS_2$ was used because of its active use as an inorganic host material.

The data in the following table is a concise representation of key results that were obtained during the Phase II research.

Table 1: Thermoelectric Power, Electrical Conductivity and Associated ZT Calculation for Conducting Polymer, Inorganic Host, & Conducting Polymer/Inorganic Host Composites at 300K

Entry	Sample ^{a,b}	σ (S/cm)	Seebeck Coefficient (μ V/K)	ZT ^c
1	V ₂ O ₅	0.051	-500	1.28E-3
2	V ₂ O ₅ /PPV composite	0.047	-360	6.09E-4
3	PETT	5.0E-4	+27	3.6E-8
4	PETT/V ₂ O ₅	0.03	-333	3.33E-4
5	PBTT	4.0E-4	+30	3.6E-8
6	PBTT/V ₂ O ₅	0.04	-400	6.4E-4
7	PBT/V ₂ O ₅	0.15	-525	3.7E-3
8	PHT/V ₂ O ₅	0.05	-525	1.38E-3
9	PANI-EB	NR	NR	-
10	PANI-ES	0.14	NR	-
11	PANI-ES-CSA	4.5	NR	-
12	PANI-ES-CSA/V ₂ O ₅	0.60	NR	-
13	V ₂ O ₅ on PANI-ES-CSA	0.02	-566	7.2E-4
14	PEDT partially dedoped	0.05	NR	NR
15	PEDT redoped with FeCl ₃	0.13	NR	-
16	PEDT/V ₂ O ₅	5.3E-3	-600	1.8E-4
17	LiMoS ₂	NR	NR	-
18	(1:1)V ₂ O ₅ /LiMoS ₂	0.31	\sim (-160)	7.94E-4
19	NaMoO ₃	NR	NR	NR

^a All thiophene polymers were tested in the doped state using FeCl₃.

^b All PANI samples were cast with hexafluoro-2-propanol (HFIP)

^c A value of 0.003 W/cm-K was used to calculate ZT.

PANI-EB: Polyaniline emeraldine base (undoped form).

PANI-ES: Polyaniline emeraldine salt (doped form).

PANI-EB-CSA: PANI-EB doped with camphor sulfonic acid.

PANI-ES-CSA: PANI-ES doped with camphor sulfonic acid.

PPV: Poly(phenylene vinylene)

PETT: Poly((3-ethylthio)-thiophene)

PBTT: Poly((3-butylthio)-thiophene)

PBT: Poly(3-butylthiophene)

PHT: Poly(3-hexylthiophene)

EDT: Ethylenedioxythiophene

PEDT: Poly(ethylenedioxythiophene)

During the Phase I effort, the poly-3-alkylthiophenes/vanadium oxide composites produced excellent electrical conductivities and thermopower values (Seebeck coefficients) of 1S/cm and high Seebeck coefficients, -500 to -1000 μ V/K, respectively. Work continued with these polymer composites, especially the 3-(*n*-hexyl)- and 3-(*n*-butyl)polythiophenes to hopefully reproduce and enhance these values to a point where this system could be utilized as a thermoelectric device. In addition, these polymers were evaluated alone, and found to give modest p-type Seebeck coefficients of +20 μ V/K, as reported by others in the literature. A closely related analog of the poly-3-alkylthiophenes, the poly(3-alkylthiothiophenes), with reported conductivities of 200-700S/cm, were also examined. Unfortunately, as seen from Table 1 (entries 3-8), as the electrical conductivity of the materials was increase the Seebeck coefficient dropped to vanishingly small values, thus no improvement in the corresponding zT was attained. This result is in keeping with those of researchers at TechOne, Inc., who examined dimensional polyanilines, and got the same result. As metallic conductivities are approached, the high Seebeck numbers disappear. The inherent nature of each measurement is somehow related that gains in one measurement can only be achieved at the expense of the other.

Polyaniline, in its various conducting states was also examined individually and as composites. The doped polyaniline films by themselves produced the highest electrical conductivity for this project. A value of 4.5 S/cm was measured for the polyaniline emeraldine salt doped with camphor sulfonic acid (PANI-ES-CSA). According to Table 1 (entries 9-12), PANI-EB(undoped) failed to produce any readings while PANI-ES yielded a modest conductivity of 0.14S/cm. It is important to note that none of the PANI forms produced Seebeck coefficient values of any substance.

Another trend was observed for the layered structures of PANI with vanadium oxide. When the PANI films were layered either on or under the vanadium oxide film, depending on the conductivity of the PANI, the Seebeck coefficient of the composite was seriously effected. For example, PANI-ES-CSA by itself had an electrical conductivity of 4.5 S/cm and an immeasurable Seebeck coefficient but when layered on top of V_2O_5 (entry 12), the conductivity decreased to 0.6 S/cm and the Seebeck coefficient was immeasurable. For the reverse case, the V_2O_5 cast on top of the PANI-ES-CSA (entry 13), the electrical conductivity was 0.05 S/cm and the Seebeck coefficient was -400 μ V/K. This trend suggests that the top layer was the dominant layer for the measurements, controlling the magnitude of both the electrical conductivity and Seebeck coefficient.

An important result that was obtained concerned the use of hexafluoro-2-propanol (HFIP) as a casting solvent for the polyaniline samples. HFIP appears to act as a solvent/dopant. This effect is evident as seen in Table 2, where PANI-ES-CSA cast from HFIP was compared to the traditional polyaniline solvent, n-methyl pyrrolidinone (NMP).

Table 2: Electrical Conductivity Comparison of Polyaniline Films Cast from HFIP and NMP

Sample	σ (S/cm)
PANI-ES-CSA from HFIP	4.5
PANI-ES-CSA	immeasurable

The PANI-ES-CSA cast from the HFIP produced a reading of 4.5 S/cm while the polymer cast from NMP failed to produce measurable reading.

PEDT has superior electrical properties, compared to other conducting polymers, because only 2,5 position polymerization can occur. That is, no polymerization through the three position of the thiophene ring is possible because it is blocked, thus more stereoregular structures are obtained. The results (Table 1 entry 16) show that we are able to maintain a high Seebeck coefficient, but again at the expense of the electrical conductivity. This result parallels the results of other researchers reported on previously. That is, as you approach metallic types of conductivities, the Seebeck coefficient drops dramatically. The synthesis of the PEDT used in these experiments involved extensive washing procedures to assure a clean polymer but what is also occurring is the removal of the iron(III)toluene sulfonate dopant which subsequently lowers the electrical conductivity. However, the polymer can be redoped with iron(III) chloride to give higher electrical conductivity values (entry 15).

Another part of this research involved measuring the stability of these materials. By way of example, the electrical properties of vanadium oxide and vanadium oxide/poly(phenylenevinylene) composites were measured. From Table 3, the electrical conductivity of the vanadium oxide/PPV composite was slightly higher than the vanadium oxide by itself after 180 hours under vacuum and heat treatment. Figures 1 and 2 show the electrical conductivity and thermopower of vanadium oxide with and without poly(phenylenevinylene). Both samples exhibit similar behavior over 150-300K. The incorporation of the unsubstituted poly(phenylenevinylene), whose reported conductivities have reached 10,000S/cm, with the vanadium oxide does not appear to have a positive effect on the electrical conductivity or the thermopower. The difficulty appears to be the

environmental sensitivity of the polymer during it's synthesis, especially as higher conductivities are approached.

Table 3: Electrical Conductivity and Thermopower Data for Vanadium Oxide and Vanadium oxide/poly(phenylenevinylene) Composite

Material	Electrical Conductivity (S/cm) ^a	Seebeck Coefficient (μ V/K) ^b
V ₂ O ₅	0.051	-460
V ₂ O ₅ /Polyphenylenevinylene composite	0.047	-360

^a after 180hrs of heat treatment @ 50°C under vacuum.

^b after 600hrs of heat treatment @ 50°C under vacuum.

Figure 1 Electrical Conductivity of Vanadium oxide/PPV Composite and Vanadium oxide

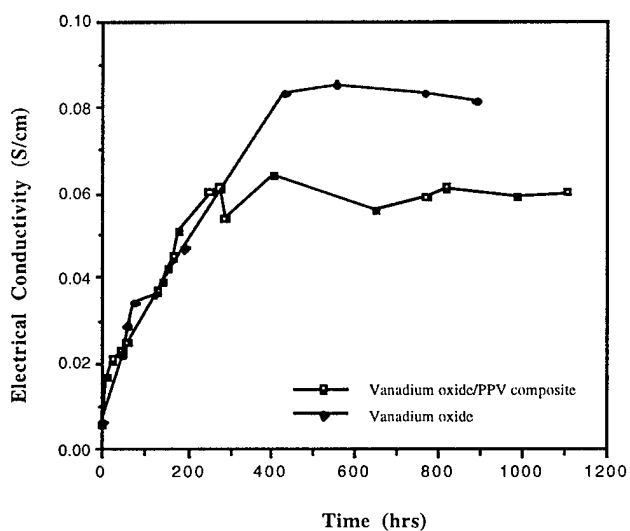
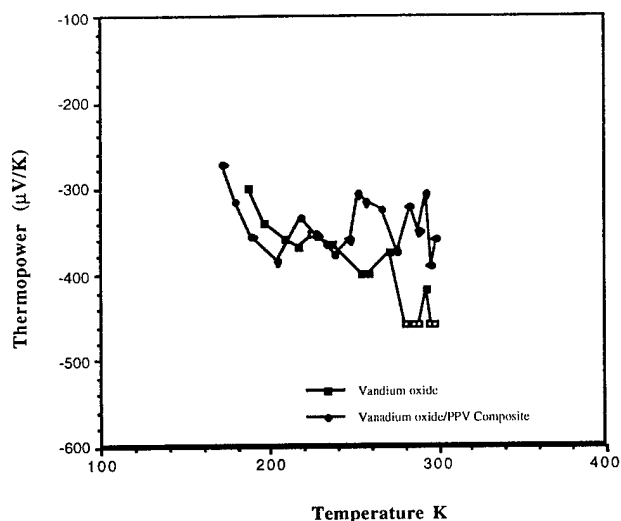


Figure 2 Thermopower of Vanadium oxide/PPV Composite and Vanadium oxide



Most of our results have shown that a delicate balance is needed in order to attain a material that has both a high Seebeck coefficient and high electrical conductivity. The polymeric films by themselves exhibit very good electrical conductivities, but when combined with vanadium oxide, the electrical conductivity of the composite is substantially lower. A possible reason for the changes lies in the thickness of the films with respect to each other. The average thickness of the V_2O_5 films are $15\mu m$, while the conducting polymer films are $\leq 1\mu m$. The results show that the thicker film dominates the thermoelectric properties.

The majority of this research dealt primarily with the vanadium oxide xerogel as the inorganic host material. Although most of the results used the procedure by Lemerle et al., we also employed a procedure by Sanchez et al. Table 4 compares the electron transport properties of vanadium oxide made by both methods.

Table 4: Comparison of Transport Properties for Different Vanadium Oxide Synthetic Procedures

Sample	σ (S/cm)	Seebeck Coefficient ($\mu V/K$)
V_2O_5 (Lemerle procedure)	0.051	-500
V_2O_5 (Sanchez procedure)	0.139	-800

3.2 Computational Methods & Results

Cape Cod Research, via the Cerius² modeling environment (program developed by Molecular Simulations Inc.), has been applying a wide array of computational methodologies to the study of materials ranging from full *ab initio* quantum mechanics (QM) to force field molecular dynamics (MD). The calculations about to be described were performed on a Silicon Graphics Indigo² (R10,000 cpu with 512 Meg Ram) Unix platform.

Three basic sets of studies were carried out. One set dealt with the conducting polymers themselves, both in their doped and undoped states. We have correlated the predicted energies of the polymer systems with the observed experimental data. This is a significant result. The second set of studies examined the adsorption of various polymers and interfacial modifiers upon inorganic surfaces, especially vanadium oxide. Not surprisingly, these studies were not as instructive. The final set of studies was probably the most interesting and examined the effect of a series of interfacial modifiers upon the resistivities of various polymer systems. The significant results of these three sets of studies will now be described.

Conducting Polymer Models and Electrical Conductivities: A Comparison of Modeling Predictions and Experimental Results

The polymers were constructed, and their energetics studied under the Universal Force Field. Classical molecular mechanics was followed by molecular dynamics (run at constant energy and volume, 300K, 100ps real time). Polymer chain lengths of 15-30 monomer units were the norm. Conformational searches (Random sampling, followed by Boltzman Jump) with energy minimization in general completed the analysis sequence. The energies of the final systems were calculated and compared with the experimental results determined independently. Two examples of predictive modeling results are representative of the overall results, one based upon polyaniline chemistry, and the other polythiophene chemistry. Entries 1-3 in Table 5 show the computed energies of polyaniline undoped, doped with HCl, and doped with camphor sulfonic acid, as well as the experimentally determined conductivity values extracted from Table 1. For the latter two cases the energies of the counterions were subtracted out after the calculations were finished.

Table 5 Computed Energy & Experimental Conductivity Comparisons

Sample	$\sigma(\text{S/cm})^1$	Modeled Energy (Kcal/mole)
1) Polyaniline (undoped)	N.R.	-30
2) Polyaniline (doped with HCl)	0.14	-56
3) Polyaniline (doped with camphor-SO ₃ H)	4.5	-76
4) PEDT (partially dedoped)	0.05	+1306
5) EDT (doped with FeCl ₃)	0.13	+1216

1. From Table 1.

2. In each case polymer chains of 15 monomer units were used. A dopant molecule was added for every three monomer units.

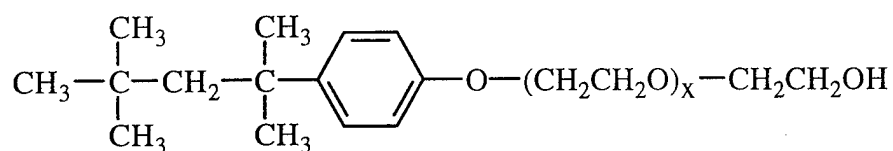
For both polymer classes the higher electrical conductivity correlated with a lower energy system as predicted by the modeling studies. The suggestion here is that modeling can be used to design and screen new polymer-dopant combinations. Work is continuing in this promising area. Printouts of two of the doped polymer systems are shown in Appendix 2.

Adsorption Modeling Studies

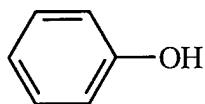
This area turned out to be a much tougher study than the first one. A number of different approaches were taken including examining a single molecule of interfacial modifier at both oxide and sulfide surfaces, multiple molecules, with and without solvent, and with and without boundary conditions. In all cases attempts were made to observe self-assembly at the surface. In no case was this observed except in the cases where the molecules were given a predisposition to one orientation or another. Appendix 2 also contains a printout of one of the most promising approaches identified in this portion of the work. Thiophenol is shown dispersed in water at a vanadium oxide surface. The aqueous phase was given a density of one, and all of the molecules could move. The solid phase atoms were fixed in space, but their charges could adjust with time. By carrying out long molecular dynamics runs on the system it was hoped that the thiol groups would eventually associate with the surface. Unfortunately, the size of systems like this (thousands of atoms) precluded real time runs longer than hundreds of picoseconds of real time. This is not long enough to observe the self-assembly phenomena. Although this approach is still promising more computer horsepower is needed to carry out long real-time calculations for very large and complex systems.

Interfacial Modifiers & Polymer Composite Conductivities

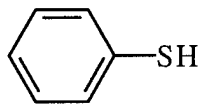
Computer simulations of semiconductors in the presence of interfacial modifiers were also run. Some of these modeling results are described in the next section. However, some experimentation was also performed *after* the modeling predictions were made. Tungsten sulfide was chosen as the model semiconductor because, as opposed to the xerogel, it was not as complex in its own right in terms of range of possible conductivities, morphologies etc. Experiments were run with a number of different IFMs including the common surfactant Triton X-100, structure **7**, and the structurally closely related triad of compounds **8-10**.



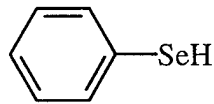
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9



10

The latter were chosen in particular because thiophenol, **9**, has been shown to readily self-organize on gold and oxide surfaces, and thus significantly change the electronic character of compositions at very low concentrations. The basic technique involved making a slurry of the WS_2 in a chloroform solution of an electronically insulating polymer, such as polycarbonate, into which the IFM was dissolved as well. Different IFMs were examined at the same molar concentrations. Films were drawn and the resistivity analyzed as a function of time and film thickness. As expected, in all cases the resistivities went down as the films dried, and then leveled off to stable values. Table 6 contains some of the most interesting results, especially when compared with the modeling predictions which follow.

Table 6 - Effect of Interfacial Modifiers on Polycarbonate Conductivities

<i>Film Composition</i>	<i>Resistivity (Kohms)</i>
Unmodified WS_2 /polycarbonate film	1000-2000
Polycarbonate + 1	2000
Polycarbonate + 2	90
Polycarbonate + 3	140
Polycarbonate + 4	200

As can be seen the surfactant did not have a positive effect on the resistivity, however the other three compounds dramatically lowered it, a significant result.

Molecular modeling was performed on two semiconducting materials, the vanadium oxide xerogel and tungsten sulfide, in the presence of various interfacial modifiers (IFMs). The basic protocol for these studies was to first build a semiconducting crystal surface and then minimize the energy of that system alone, but with the atoms constrained in space. The desired IFM was then introduced, in the presence or absence of solvent molecules, and boundary conditions imposed such that a realistic density for the organic-solvent phase (~ 1) was achieved. In essence the imposition of the boundary conditions makes the molecules perceive that they are in an infinite system, that is, edge effects are eliminated. The charges on all of the atoms were allowed to fluctuate according to the parameters of the simulation, while only the locations in space of the IFM/solvent atoms were permitted to change. The energies of the composite systems were then minimized using molecular mechanics, and then subjected to long molecular dynamics runs, generally simulating at least 100ps of real time, and usually more. Each of these dynamic runs were then followed by a second minimization process.

Although the absolute values of the energies obtained by the simulations are probably not meaningful in the real world, the calculated energy trends were as follows:

$$1 \ll 4 < 3 < 2$$

This is the same trend as observed in the experimental results of Table 7. More negative energy values suggest greater system stability, which may be in keeping with the higher resistivity values. In fact, this is also consistent with what is known about semiconducting systems in general. As resistivity goes up, and conductivity thus down, chemical stability improves significantly.

In a second simulation study the solubility of polyaniline was modeled in a number of solvents. The notoriously insoluble polyaniline was found to be soluble in hexafluoro isopropanol (HFI). Modeling using the blends module of the Cerius² software basically constructs phase diagrams of two component systems and predicts compatibility. In fact, the modeling predicted polyaniline (as a fifteen unit polymer) to be compatible with HFI, while not being compatible with plain isopropanol, acetone or CHCl_3 . Thus it proved

possible to use this tool to examine solubility parameters of different polymers in various solvents.

Computer simulations have correlated interfacial modifier structure with system energetics for some semiconducting systems and was used as a predictive tool. The trends observed in the modeling were then observed in actual experimental systems compositions prepared and evaluated in the laboratory. A correlation of lower simulation system energetics with higher experimental resistivities was in fact realized.

3.3 Experimental Procedures

3.3.1 Conducting Polymer Synthesis

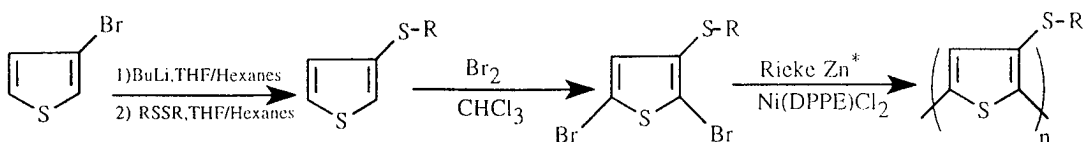
Poly(3-(alkyl)thiophene) alkyl=butyl,hexyl

In an oven dried three neck round bottomed flask(250mL), equipped with magnetic stirring, dropping funnel, nitrogen inlet, and reflux condenser, was dissolved 3-bromothiophene (3.0g,18.0mmol) in dry ether (10mL). To this a solution of appropriate alkyl Grignard reagent in dry ether was added dropwise under nitrogen atmosphere. After addition was complete, the reaction mixture was refluxed for 24 hours. The solution was cooled and acidified with 10%HCl to quench the excess Grignard reagent. The product was extracted with ether, washed with water, and dried over MgSO₄. The product was filtered and the solvent removed under vacuum. Yield=50-60%.

Synthesis of Poly(3-(alkyl-thio)thiophenes) alkyl=butyl,hexyl

This procedure was adapted from Reike et al.¹⁷ To a solution of 3-bromothiophene (0.02mol) was added n-butyllithium (0.021mol, in hexane) in hexane (30mL) at -40°C under nitrogen. THF (3mL) was added via syringe. After approx. 20 min, an additional 10mL of hexane was added and the reaction was warmed to room temperature. The resulting mixture was transferred to a second flask containing the alkyl disulfide in 20mL hexane. The reaction was worked up with NH₄Cl(aq.) (20mL) and the organic layer was extracted with ether. The solvents were removed and purified by chromatography over silica gel using hexane. The 2,5-dibromo-alkylthio-thiophene is then brominated by reacting the alkylthio-thiophene with bromine and chloroform. The regioregular head to tail polymer is then prepared by reacting the dibromo-alkylthio-thiophene with Rieke activated

Zinc in the presence of nickel catalyst, Ni(DPPE)Cl₂. The following reaction summarizes the procedure.



Synthesis of Poly(ethylenedioxythiophene) (PEDT)

Poly(ethylenedioxythiophene) (PEDT), delivered as a two component system(monomer and oxidant) and commercially available under the tradename Baytron® (Bayer Corp.), was synthesized by mixing 4 parts oxidant to 1 part monomer. The resultant dark blue-black solids were washed with methanol extensively to remove unreacted oxidant. The solids were then dissolved in an appropriate solvent and cast into films.

Synthesis of undoped Polyaniline emeraldine-base (PANI-EB):

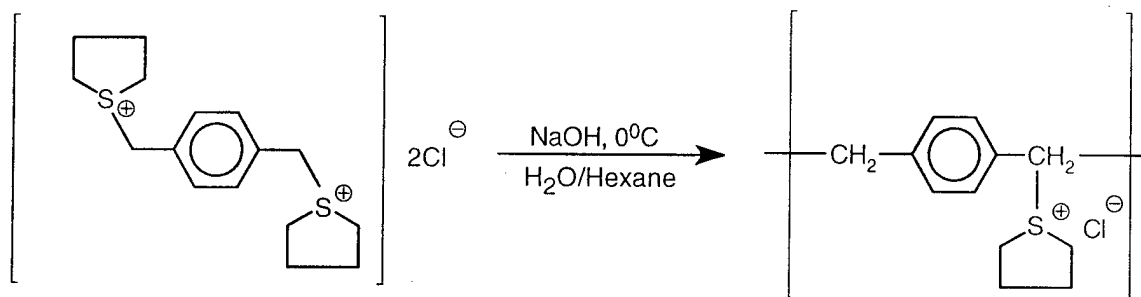
Polyaniline emeraldine base (PANI-EB) was prepared by dedoping the polyaniline emeraldine salt (PANI-ES), Aldrich Chemical Co.. The green colored PANI-ES was stirred with 1.0M NH₄OH for 2 hours then filtered and washed with copious amounts of distilled water, methanol, then diethyl ether. The now dark blue-black polymer was then vacuum dried to remove excess solvent. The polymer was then dissolved in hexafluoro-2-propanol (HFIP) and dark blue-black films were cast from this solution.

Synthesis of doped Polyaniline emeraldine base (PANI-EB) and Polyaniline emeraldine salt (PANI-ES) with camphor sulfonic acid:

The PANI-EB and PANI-ES powders were doped with camphorsulfonic acid by mixing the polymer in a 2:1 mole ratio with the acid. For example, 3.3mmol of camphor sulfonic acid was first dissolved in 10mL of hexafluoro-2-propanol (HFIP). This solution was then added to a polymer solution containing 6.6mmol of polymer dissolved in 20mL of HFIP. The solution was then mixed vigorously for 48 hours then filtered through a 0.2µm Poly(vinylidene fluoride) filter to remove any particulates. Dark blue-green films were then cast from this solution.

Synthesis of soluble precursor of poly(phenylene vinylene)

In a round bottom flask, *p*-xylylenebis(tetrahydrothiophenium chloride) (0.01 moles) was made into a suspension in a mixture of 20mL of de-ionized water and 80mL of hexane. The suspension was deaerated by purging with nitrogen. Simultaneously, sodium hydroxide (0.01 moles) was dissolved in 20mL of deionized water and then purged with nitrogen. Both solutions were cooled in an ice-water bath to 0°C, before they were mixed. The reaction mixture was stirred at this low temperature, under N₂ atmosphere, for one hour. The hexane was decanted off and the reaction mixture neutralized with 1M hydrochloric acid. Nitrogen gas bubbled through this solution to remove any remaining hexane. The solution was then purified by dialysis. The following reaction summarizes the procedure.



Vanadium oxide (V_2O_5)-I

The following is a representative procedure for making a vanadium pentoxide xerogel solution as adapted from Lemerle et.al.¹ In a 250mL beaker, 1.5g of NaVO_3 was added to 100mL distilled water and stirred. Approximately 30g of Dowex 50WX2-100 ion exchange resin was added slowly to the mixture in 10g increments. A color change was observed from cloudy white to orange. An additional 1.5g of NaVO_3 was added to facilitate the completion of the reaction. Stirring was continued at such time the solution turned dark red. The ion exchange beads were then vacuum filtrated and the filtrate stirred for n additional 5-6 hours. The solution was then cast and air dried to form the xerogel.

Vanadium oxide (V_2O_5)-2

The following procedure was adapted from Sanchez, C. et al.¹⁶, to make a vanadium oxide xerogel solution. DI water was added to vanadium tri-n-propoxide oxide until solution turned yellow to a dark red color. Solution was stirred vigorously for 1 hour and cast into films. Gelation begins after a few hours. Appropriate dilutions were made with DI water to make films.

Molybdenum disulfide ($LiMoS_2$)

In a 500mL 3-neck round bottom flask was charged 1.0g of MoS_2 (<2 μ m, 0.00625mol), under nitrogen flow. Via syringe, 9.5mL (0.238mol) of 2.5M n-Butyl lithium in hexane was added and stirred for 48 hours. The mixture was then added to 150mL of ice cold deionized water to quench the excess n-BuLi. The resultant $LiMoS_2$ dispersion was then vigorously stirred and ready for use.

Molybdenum trioxide ($NaMoO_3$)

In a 250mL 3-neck round bottom flask, 2.5g of MoO_3 was suspended in 125ml of DI water. Nitrogen gas was bubbled through the solution for 1/2 hour. A dry mixture of 1.0g of $Na_2S_2O_4$ and 20.0g of $NaMoO_4$ was added and stirred with N_2 bubbling. The mixture was then stirred for 3 hours. The mixture was then filtered by vacuum and washed with DI water until filtrate became clear. The resultant solids were metallic blue-black. The solids were redispersed in DI water and cast out into films.

3.3.3 Composite and Layered Composite Synthesis

The majority of the electric conductivity and thermoelectric testing was performed on layered composite samples. The general procedure for these samples was as follows: The alumina substrate was masked off with Teflon tape to expose a surface area of only 0.500" X 0.2500". A solution of desired material was then either spin cast or drop cast onto the surface and allowed to dry appropriately. Additional layers of the same or different materials were applied in the same manner. For specific composite mixtures, the following procedure(s) was employed:

Vanadium oxide/Polyphenylenevinylene(PPV) Composite Synthesis

Molar amounts of the aqueous V_2O_5 xerogel solution and aqueous PPV precursor were stirred together under inert atmosphere. Solution was deoxygenated by a freeze-thaw method under vacuum and then film cast. The water was removed by bubbling inert gas over the films and then the films were slowly heated to 220°C (approx. $25^\circ\text{C}/\text{hours}$) under high vacuum.

(1:1)Vanadium oxide/ $LiMoS_2$ Composite Synthesis

We were unable to cast films of $LiMoS_2$ by themselves, therefore, V_2O_5 was then added to improve the film forming capabilities. 5.0mL of the $LiMoS_2$ solution was added to 5.0mL of V_2O_5 solution and stirred vigorously for 1 hour. Solution become dark reddish black. Films were then cast out on alumina wafer substrates and dried in a controlled atmosphere glove box.

3.3.4 Electrical Conductivity and Thermopower Measurements

Electrical conductivity and thermopower samples were cast on polished 99.6% alumina substrates metallized with the gold pattern illustrated below. Each substrate is 1.00" x 0.500" and each sample size is 0.500" x 0.2500" and the thickness is a function of the type of material. Sample preparation involved first masking off the gold pads with Teflon tape and spin coating the sample using a Headway Research, Inc. spin coater. Removal of the mask is the final step in sample preparation. The sample that remains covers only the gold lines and not the pads which serve to make contact to the current source and/or multimeter. In most cases, multiple layers of material(s) are applied.

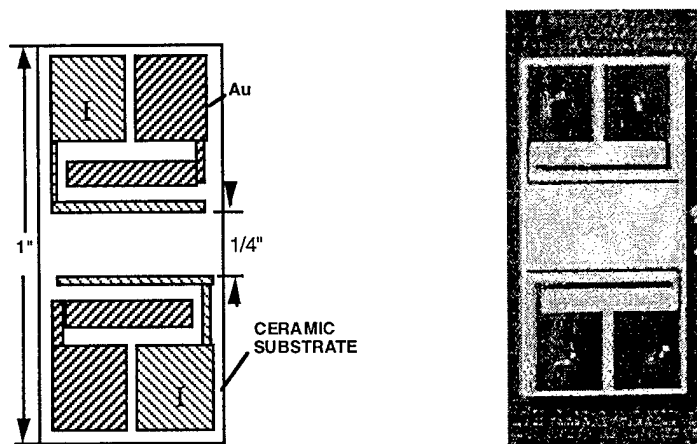


Figure 4 Electrical conductivity and Thermopower Test Substrate

Electrical Conductivity

The electrical conductivity measurements were made via the four point probe method. An electrical current from an external current source (Keithley Model 224 Programmable Current source) is passed between the two outer gold wires while the voltage drop is measured between the two inner wires (precisely 0.2500" apart) with a Hewlett Packard digital multimeter (HP 3468 A/B). Voltage measurements were made at three or more current levels to ensure that the current-voltage behavior was ohmic.

Thermopower

In order to measure the thermoelectric power, the test apparatus shown in Figure 4 was designed and built as part of the Phase I work. It consists of a vacuum tight through connector which allows connection to two thermocouples and six lead wires to a sample holder. The thermocouples are of fine gauge and made from relatively poor heat conductors (chromel-alumel) and extend almost two feet from the through connector to the junction. This minimizes thermal flux to the junction via the leads.

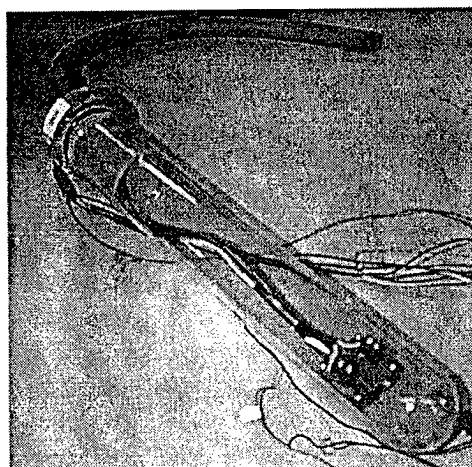


Figure 5 Thermopower Measuring Device

The body of the sample holder consists of a 1"x 1"x 0.25" block of copper which is milled in one direction to partially thermally isolate one side from the other. Perpendicular to this slot is milled a groove in which are epoxied with silver-filled epoxy two identical thermoelectric coolers. These are electrically connected in series and mounted so that one

has the hot face up and the other has the cold face up. The thermoelectric coolers are driven by a DC power supply (BK Precision). The test sample fits snugly over these surfaces so that the gold lines and pads can be both heated and cooled from underneath. Temperature differences between the gold test lines can be set precisely by the DC power supply to set the current flowing through the thermoelectric coolers while the assembly as a whole heats up at a rate which is also proportional to this current.

Electrical connections from the test sample's gold pads to the four lead wires are made via balls of solder which protrude slightly below a sheet of perforated circuit board. Temperature measurements are made via two thermocouple junctions. Small disks of mica are placed on the board and the junctions wet with five minute epoxy. The wet junctions were forced through the circuit board holes so that they touched the mica. After the epoxy set, layers of mica were peeled away to leave the epoxied junction only a few mica layers from the surface. This procedure leaves the junctions above the plane of the circuit board and greatly reduces the thermal path from the junction to the test sample. It also insulates the junction from the sample. The junctions are located directly over the sample film which covers the inner pair of gold lines. This minimizes measuring errors due to temperature changes across the ceramic support.

The apparatus was assembled and the thermopower measurements were performed. The system is vacuum tight and can be placed in liquid nitrogen or heated to high temperatures. The maximum heating rates were about 10°C per minute and depended on the dc current fed to the thermoelectric coolers. The test apparatus is symmetrical so that rotating the test sample 180 degrees in the holder reverses the hot and cold side without any changes in geometry. This provided an internal check of the thermocouple measurements.

The four lead wires are connected to a Hewlett Packard digital multimeter (HP 3468 A/B), which has four wire measuring capability as well as $1\mu\text{V}$ sensitivity. The thermocouples are connected to a commercial microprocessor circuit for directly converting voltage to temperature (Omega Model HH22). Thermopower measurements were performed from 100 to 300K. A temperature gradient of 0.5°C was maintained throughout the test and the voltage measure as a result of the temperature difference.

4.0 CONCLUSIONS

It was hoped that during this Phase II effort zT values significantly greater than one could be attained. This did not occur. However, a number of significant results were obtained as follows:

- * Highly stable and reproducible thermopower values of -500 to -800 $\mu\text{V/K}$ were consistently obtained.
- * Electrical conductivities were improved to up to 4.5S/cm.
- * Upon attaining high electrical conductivities, the Seebeck coefficient dropped dramatically.
- * The thickness of materials dramatically affects the thermoelectric properties.
- * The materials were easily processable and the thicknesses of layered materials can be accurately controlled.
- * Molecular modeling was used to correlate electrical conductivity with polymer/dopant structures.
- * Molecular modeling was used to predict the effects of interfacial modifiers upon polymer-inorganic filler electrical properties.

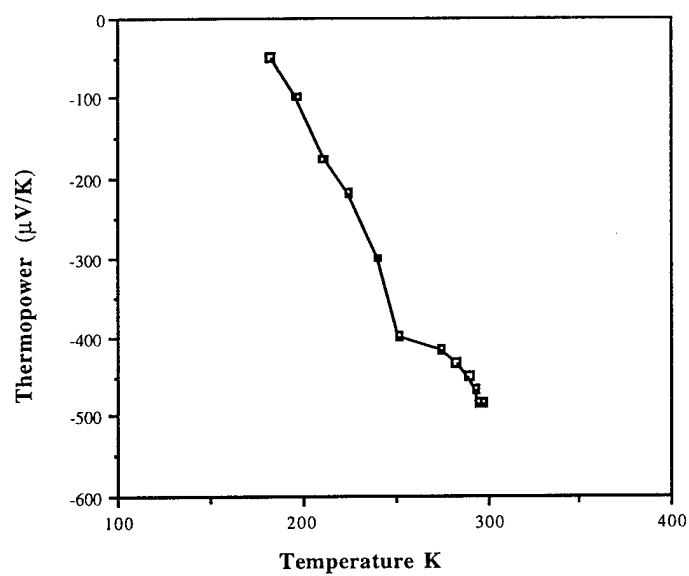
4.0 REFERENCES

1. Lemerle, J.; et al.; *J.Inorg. Nucl. Chem.* **1980** 42 17.
2. Sanchez,C.; et al.;*Better Ceramics Through Chemistry III* , ed. Brinker, J . **1988**, 93.

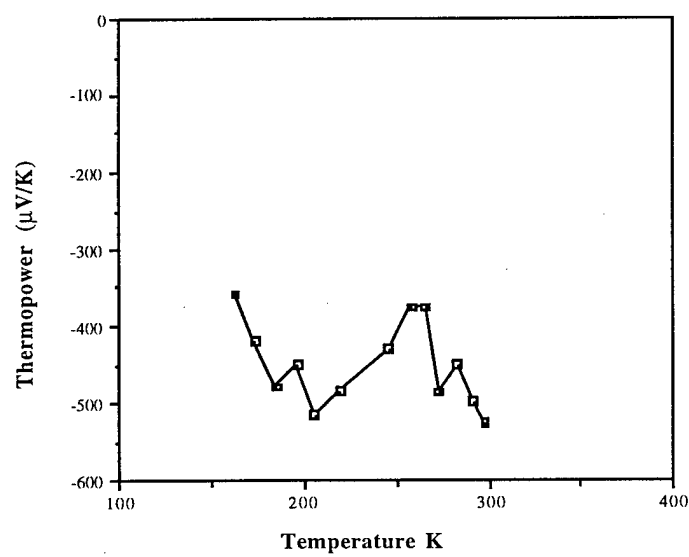
APPENDIX 1

Thermopower Graphs

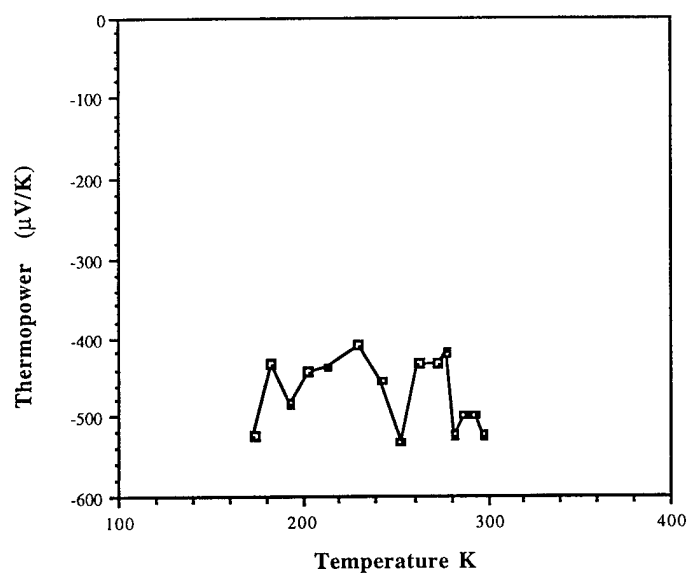
Thermopower of Vanadium Oxide Entry 1



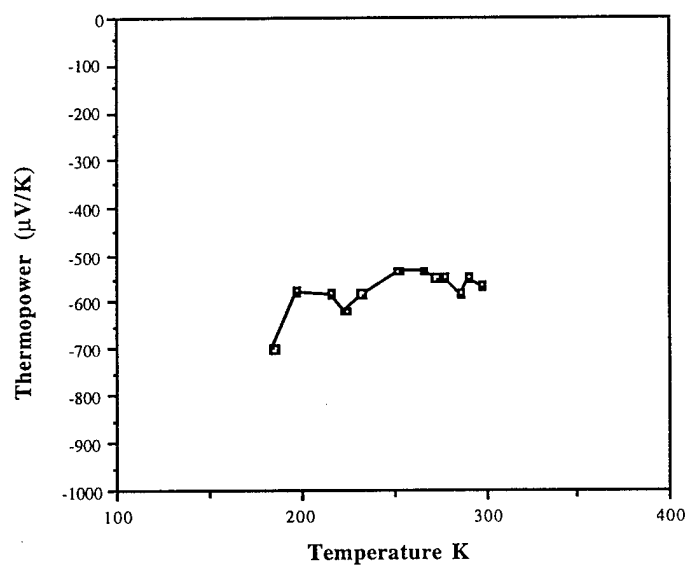
Thermopower of Poly(3-butylthiophene)/Vanadium oxide Entry 7

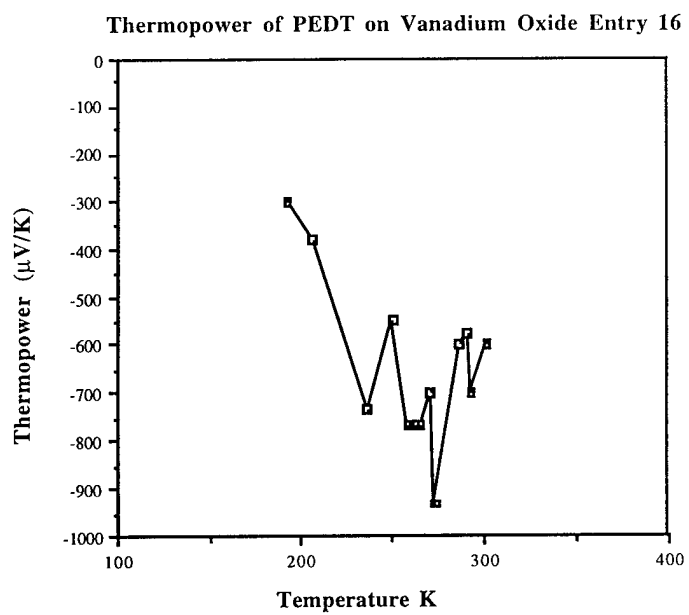


Thermopower Poly(3-hexylthiophene)/Vanadium oxide Entry 8



Thermopower Vanadium Oxide on PANI-ES-CSA Entry 13





APPENDIX 2

Modeling Printouts

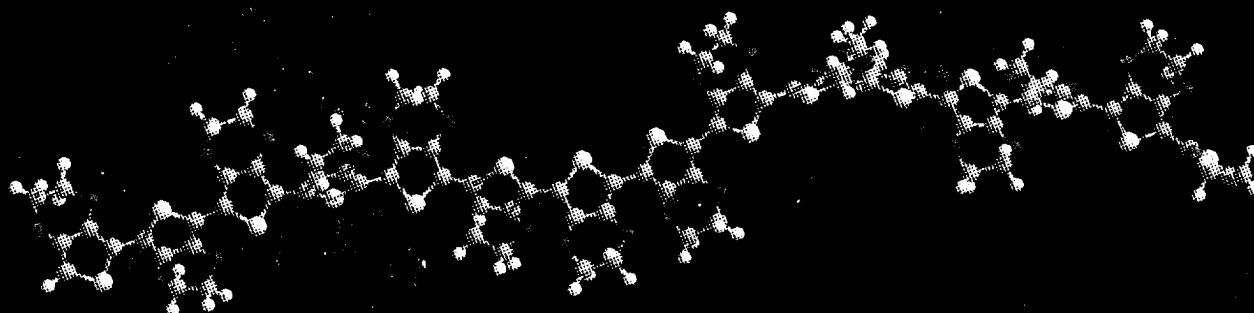


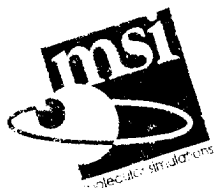
Cerius²

Title: Poly-3,4-dioxythiophene Doped with HCl

Author: Cape Cod Research, Inc.

Date: Fri May 22 09:53:41 1998



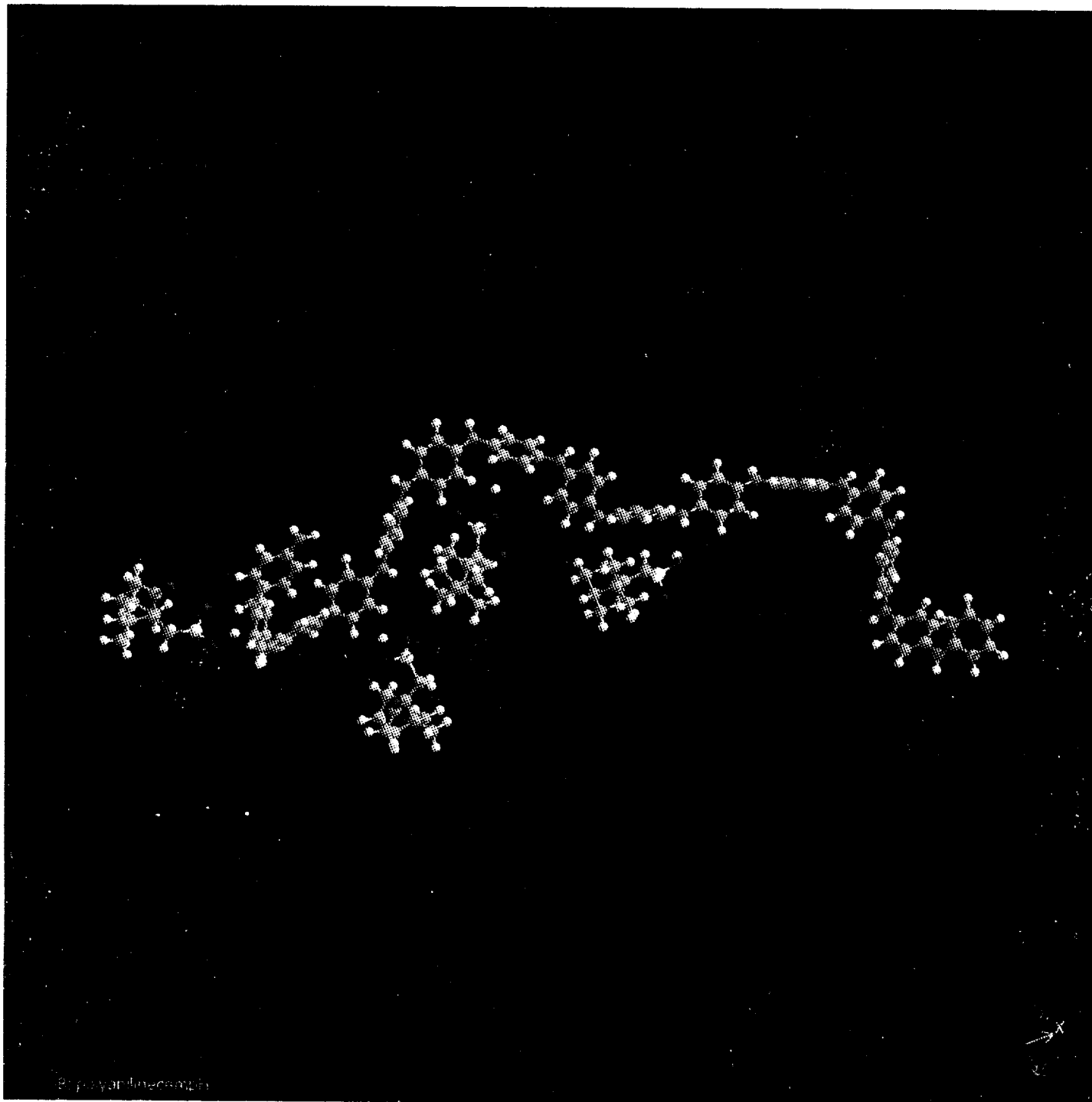


Cerius²

Title: Polyaniline Doped with Camphor Sulfonic Acid

Author: Cape Cod Research, Inc.

Date: Mon May 18 11:35:42 1998



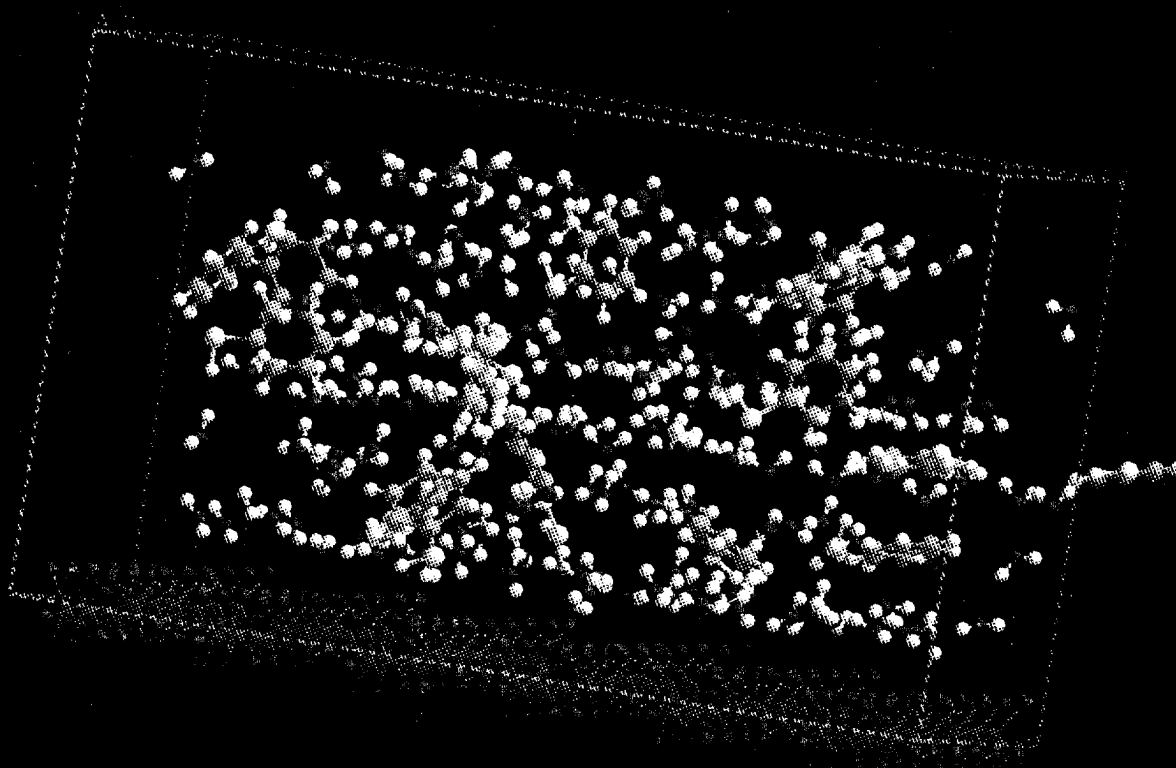


Cerius²

Title: Hydrated Thiophenol on VxOy Xerogel Surface

Author: Cape Cod Research, Inc.

Date: Fri May 22 09:57:54 1998



17. thioVxOyBox

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